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Condensation of 2-pyridylmethyllithium nucleophiles and pyridine electrophiles as a convenient synthetic route to polydentate chelating N-donor ligands

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Abstract

Condensation of 2-pyridylmethyllithium or (6-methyl-2-pyridyl)methyllithium nucleophiles and pyridine, 2-picoline, or 4-tert-butylpyridine as electrophiles leads to new polydentate N-donor ligands, methyl-, tert-butyl-substituted tripyridinedimethanes, or to tripyridinedimethane itself, in good or high yields. Depending on the reagent ratio, solvent used, and reaction conditions, the corresponding intermediate dipyridinemethanes can be minor by-product or major products of the condensation. In contrast to 2-pyridylmethyllithium, lithiated 2-isopropylpyridine does not react with pyridine electrophiles. Vice versa, nucleophilic substitution at the C(2)-pyridine carbon of 2,2-bis(2-pyridyl)propane with 2-pyridylmethyllithium takes place to produce products of condensation of 2-isopropylpyridine and dipyridylmethyllithium. DFT calculations of the Gibbs free energies of reactions combined with pKa values of the CH-acids involved help to explain the reactivity observed.

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Keywords

(6-methyl-2-pyridyl) methyllithium, 2,6-lutidine, 2-picoline, 2-pyridylmethyllithium, 4-ter--butylpyridine, C-C bond cleavage, Condensation, DFT calculations, Dipyridinemethanes, Gibbs free energy of reaction, Pyridine, tripyridinedimethanes